

ATMOS Stratospheric Deuterated Water and Implications for Troposphere-Stratosphere Transport

Elisabeth J. Moyer¹, Dr. William Irion², Yuk L. Yung¹, and Michael R. Gunson³

Received _____; accepted _____

Short title: ATMOS DEUTERATED WATER AND TROP-STRAT EXCHANGE

¹Division of Geological and Planetary Sciences, California Institute of Technology

²Division of Chemistry and Chemical Engineering, California Institute of Technology

³Jet Propulsion Laboratory, California Institute of Technology

Abstract,.

The isotopic composition of stratospheric water vapor is used as a tracer for the convective history of air injected into the stratosphere. Stratospheric profiles of H_2O , CH_3D , and CH_4 from the ATMOS instrument, obtained over four missions from 1985-1994, are used to determine the initial deuterium-to-hydrogen ratio of water vapor entering the stratosphere. We find that the initial δD of stratospheric water is -680 ± 80 (68% loss of deuterium), consistent with extrapolations from previous measurements at higher altitudes. This value is consistent over latitude and time; we see no evidence for latitudinal - or seasonally-varying transport mechanisms. Simulations with a multi-phase isotopic cloud model show that stratospheric water is less depleted than would be expected for simple ascent in the upper troposphere. The observed isotopic composition of stratospheric water can be reproduced only through non-equilibrium processes such as evaporation of lofted cloud ice or condensation in highly supersaturated conditions. As both these processes can occur only in cases of extremely high updraft velocities, we conclude that the majority of troposphere-stratosphere exchange must be associated with rapid convection to at least upper tropospheric levels,

Introduction

The extreme dryness of the stratosphere is generally assumed to be the result of condensation at the coldest temperatures that air parcels experience during their ascent into the stratosphere. The temperatures thus inferred have historically been used as evidence of the mechanism by which troposphere-stratosphere transport occurs. *Brewer* [1949] first proposed that air moves into the stratosphere by large-scale ascent in the tropics, where the tropopause is highest and coldest. More accurate measurements of tropical tropopause temperatures since that time have led to the understanding that troposphere-stratosphere transport cannot be as widespread and continuous as *Brewer's* proposal implied. As the mean tropical tropopause is too warm to freeze-dry air to the observed stratospheric mixing ratios, injection of air into the stratosphere must be more episodic or more localized [*Reid & Gage* 1981]; *Newell & Gould-Stewart* 1981].

The temporal and spatial scales of troposphere-stratosphere transport are not well-constrained, however. Transport has been proposed to occur by ascent over the course of a season over the $\approx 10^7 \text{ km}^2$ region of the tropics where the tropopause is coldest [*Newell & Gould-Stewart* 1981; *Holton* 1995]. Alternatively, transport may occur in numerous isolated convective events during which the local temperature structure is temporarily perturbed, with scales of several to 10^3 km^2 and days to hours, [*Danielsen* 1982, 1993; *Potter & Holton* 1994]. observations of stratospheric water vapor content have not provided a means of distinguishing between the possible scales and speeds of transport.

While all proposed mechanisms for troposphere-stratosphere transport are constrained to produce the observed stratospheric dryness, they may involve different means by which air is dehydrated. In all models requiring transport by gradual ascent, dehydration occurs by simple cold trapping at the tropopause. Models of transport by localized convective events may involve more complicated dehydration mechanisms. Convective cumulus towers which penetrate the tropopause and deposit

air in the stratosphere above it can carry with them enormous quantities of water as ice: near-tropopause ice to vapor ratios can exceed 100 [*Knollenberg et al. 1993, 1982*]. The final water vapor mixing ratio produced may then be the result of a combination of condensation and evaporation. Determination of not only the final water content of stratospheric air, but of the process by which that content is reached, can thus serve to discriminate between these theories, and can provide insight into the larger question of how air is exchanged between troposphere and stratosphere.

We propose that the isotopic composition of stratospheric water vapor is a useful tracer for this purpose. Because water isotopic composition is altered by all phase changes, stratospheric water carries with it an isotopic record of the condensation and evaporation experienced by each air parcel that crosses the tropopause. When several phases of water are present in thermodynamic equilibrium, the heavier isotopes will partition preferentially into liquid or solid water, leaving the vapor depleted in deuterium (and heavy oxygen) and the condensate enriched. The degree of preference is termed the fractionation factor, defined as

$$\alpha = \frac{(D/H)_{\text{vapor}}}{(D/H)_{\text{condensate}}}.$$

(This paper discusses only fractionation of 111^{16}O vs. 112^{16}O , and α is used to indicate the fractionation factor for these species only.) For deuterated water, α is a strong function of temperature, ranging from 1.08 at room temperature, an 8% enrichment of liquid relative to vapor, to over 1.4 for ice condensation at the ≈ 190 K tropical tropopause [*Majoube 1971; Merlivat & Nief 1967*]. As water condenses and is removed from an air parcel, the residual vapor is progressively lightened as deuterated water is preferentially removed. The stratosphere, with a water vapor concentration four orders of magnitude less than that at sea surface, should be highly depleted in deuterium. However, the exact degree of depletion, and the variations in that depletion, should be a function of the particular process by which stratospheric air has been dehydrated.

ATMOS observations of the isotopic composition of entering stratospheric water

observations of stratospheric deuterated water by the Atmospheric Trace Molecular Spectroscopy (ATMOS) FTIR instrument over the last decade provide the first large database of isotopic compositions that can be applied to the problem of troposphere-stratosphere exchange. There have been few previous reported measurements of H_2^{18}O and H_2^{17}O in the lowest stratosphere, where accurate spectroscopic measurement of both species is difficult, and none in the tropics, the presumed source region for stratospheric air and water. Water vapor in the mid-latitude stratosphere has been observed to be strongly depleted of deuterium, but with deuterium content increasing with altitude from a $\delta\text{D}_{\text{water}}$ of approximately -600 at 20 km to -350 to -450 at 35 km. [Rinsland *et al.* 1991, 1984; Dinelli *et al.* 1991; Carli and Park 1988; Pollock *et al.* 1980]. (Isotopic composition is given in δ notation, where $\delta\text{D}_{\text{water}}$ is the fractional difference, in permil, of the D/H ratio of the measured water from that of standard mean ocean water (SMOW), at 1.5576×10^{-4} [Hageman *et al.* 1970].) This increase has been presumed to be the result of methane oxidation. Because stratospheric methane is far less depleted of deuterium than is entering stratospheric water, its oxidation produces relatively heavy water which enriches stratospheric $\delta\text{D}_{\text{water}}$ [Elhail 1973; Irion *et al.* this issue; Rinsland *et al.* 1991].

The ATMOS instrument is particularly suited for the study of stratospheric water isotopic composition because it provides near-simultaneous measurements of all the major stratospheric hydrogen- and deuterium-bearing species, CH_4 , CH_3D , H_2^{18}O , and H_2^{17}O , allowing the estimation and subtraction of this methane-derived H_2^{18}O and H_2^{17}O . Because there are no other processes which can significantly affect the isotopic composition of water once it reaches the generally undersaturated stratosphere, this provides an effective determination of the original isotopic composition of water vapor

as it enters the stratosphere. Even high-altitude and -latitude data can thus provide isotopic information about near-tropopause processes.

This analysis uses data from all four ATMOS missions from 1985 - 1994, a total of 71 occultations in which HDO, H₂O, and CH₄ were retrieved (filters 2, and 9), and 68 in which CH₃D was retrieved (filter 3). Occultations in the polar vortices, where dehydration on polar stratospheric clouds produces additional isotopic effects, have been excluded. Latitudinal coverage is near-global (24% tropical, 18% mid-latitudes, 58% high latitudes), allowing examination of potential changes in δD due to differing injection mechanisms in different locations. The ATMOS instrument, coverage, and data reduction procedure are described in detail elsewhere [Farmer 1987; Gunson *et al.* this issue; Irion *et al.* this issue].

Methane-derived contributions of HDO and H₂O at each data point are estimated by using the relationships between deuterated and undeuterated methane and water in the lower stratosphere established by Irion *et al.* and Abbas *et al.* [this issue]. Each lost molecule of methane is assumed to produce two water molecules, and each lost molecule of CH₃D one of HDO:

$$[HDO]_{x,corrected} = [HDO]_0 - ([CH_3D]_0 - [CH_3D]_x)$$

$$[H_2O]_{x,corrected} = [H_2O]_0 - 2 ([CH_4]_0 - [CH_4]_x)$$

(Since the concentrations of the deuterated species are four orders of magnitude less than the undeuterated ones, the contribution to, for example, H₂O by oxidation of CH₃D is negligible). Initial concentrations of CH₄ and CH₃D are taken as 1.7×10^{-6} and 1.0×10^{-9} , respectively, from WMO [1994] and the fitted $\ln[CH_3D]/\ln[CH_4]$ relationship of Irion *et al.* [this issue] derived from the filter 3 data. CH₃D concentrations are inferred from observed CH₄ in filters 2 and 9 using this relationship. No assumptions are made as to the initial concentration of water entering the stratosphere.

Figure 1a shows measurements of the (uncorrected) isotopic composition of stratospheric water from all four ATMOS missions. The previously observed increase in

deuterium content with altitude is evident. Figure 1b shows the same data, corrected for the methane contribution. There is no trend in composition with altitude, indicating that the methane contribution has been effectively removed. The mean isotopic composition of stratospheric water is highly depleted, with a δD of -680 ± 80 per mil, (weighted mean of all extravortex observations from 18-32 km; error represents 10 of the distribution + systematic error.) That is, the mean water entering the stratosphere has lost 68% of its deuterium. There is no significant variation in δD_{water} with mission, filter, or latitude.

Implications of mean δD_{water}

To explore the implications of the stratospheric water isotopic signature, we have developed a multi-phase cloud model that computes isotopic trajectories during the ascent of air to the tropopause. The model represents the one-dimensional, pseudoadiabatic lifting of air parcels, with the concentrations and isotopic compositions of vapor, liquid, and ice tracked throughout. Air parcels are stepped upward until the water vapor mixing ratio equals the ATMOS-observed average lower stratospheric value of 3.8 ppm [Abbas *et al.*, this issue]. (The model results are robust with respect to this value; possible seasonal variations in water vapor of $\pm 20\%$ would produce only minor isotopic variations). Isotopic effects include fractionation during initial evaporation of seawater, during condensation of liquid and ice, and during the conversion of liquid to ice as the cloud glaciates. Cloud liquid is allowed to re-equilibrate with cloud vapor, while ice is effectively removed from the vapor. Free parameters of the model are: surface temperature and relative humidity, the temperatures of the onset of ice nucleation and the completion of glaciation, a factor representing the relative importance of droplet freezing to evaporation and re-deposition during glaciation, the degree of supersaturation over ice in the final stages of ascent, and the fractional precipitation (or lack thereof) in all condensing stages. Although simplified, the model captures the full range of possible

conditions for a simple convective updraft.

In the first set of model runs isotopic partitioning was assumed to occur at thermodynamic equilibrium in all stages, with the temperature dependence of α taken from *Majoube [1971]* and *Merlivat & Nief [1968]*. Figure 2a shows the full range of isotopic trajectories possible under these conditions. All model-generated final isotopic compositions at the tropical tropopause are considerably lighter than those observed for stratospheric water. While stratospheric water vapor is highly depleted of deuterium, it is less depleted than would be expected for the amount of dehydration required.

Although some model parameters can substantially alter vapor isotopic compositions at lower altitudes, where liquid water is present, all trajectories essentially converge during the nearly 7 km of ascent in ice-only conditions from the homogeneous nucleation point of water at 233 K to the tropical tropopause at ≈ 190 K. Those last kilometers of ascent strip out virtually all deuterium from the vapor: water vapor concentration must drop by a factor of over a hundred, with strong fractionation at $\alpha = 1.3 - 1.4$, so vapor D/H must drop by over 80% over this altitude range alone. Even if no depletion occurs until the onset of ice condensation, the final δD under these conditions would still be less than -800. Some other mechanism is required to produce the more enriched water observed in the stratosphere.

The deuterium content of stratospheric water can be increased only if we postulate that 1) air parcels in this 10-17 km region receive additional contributions from sources that are not in equilibrium with the vapor, or 2) that the isotopic fractionation experienced is weaker than equilibrium values imply. The first postulate requires the presence of lofted cloud ice, the only plausible source for non-equilibrated water in the upper troposphere or lower stratosphere. While liquid water can rapidly exchange and equilibrate with its environment, the isotopic composition of ice remains essentially fixed [*Jouzel & Merlivat 1984*]. Ice particles carried upwards from their altitudes of condensation thus preserve far heavier isotopic compositions than would be expected

from their surrounding vapor, and, if subsequently evaporated, can serve to enrich the vapor D/H ratio.

The second postulate- that isotopic fractionation has been reduced - is possible in highly supersaturated air parcels, where kinetic effects prevent the vapor and condensate from achieving their equilibrium isotopic partitioning. Because the diffusivity of H_2O is greater than that of HDO , the vapor near the condensation nuclei becomes lighter than the bulk vapor, and the effective fractionation of condensing water is lessened. A full treatment of this effect is given in *Jouzel & Merlivat [1984]*. Figure 2b shows isotopic trajectories calculated using this kinetic fractionation, for a range of supersaturations. Because the condensing material extracts less deuterium, the residual vapor remains heavier; at supersaturations of 1.5 to 2 (150 - 200 %), depending on convective parameters, sufficient deuterium is left at the tropopause to match the observed stratospheric isotopic composition.

Either of these postulates required to enrich stratospheric water in deuterium is possible only in convective systems. Supersaturations of 1.5 to 2 can be sustained only by updraft velocities typical of the strongest cumulus cores; in steady state, 30-40 m/s for the range of ice particle size distributions observed in tropical near-tropopause cloud systems [*Knollenberg et al. [1993, 1982; Rogers & Yau 1989; Pruppacher & Klett 1980]*. Ice crystal evaporation, on the other hand, can significantly alter the isotopic composition of vapor only if the ice crystals are substantially out of equilibrium with that vapor. Ice must thus evaporate at altitudes significantly higher than its level of condensation, again a condition possible only in strong convective updrafts. Furthermore, any enrichment of water vapor in ascending air parcels must occur near the tropopause in order for the enrichment to persist as air rises and dehydrates to stratospheric values. The strong fractionation at upper tropospheric temperatures means that without a non-equilibrium source of deuterium, water is depleted from the troposphere to observed stratospheric D/H in less than three kilometers of ascent. Regardless of which

mechanism is responsible for the enrichment of stratospheric water, the mean air that enters the stratosphere must have experienced convective conditions in the uppermost troposphere.

Variability of δD_{water}

The mean stratospheric δD_{water} is largely uniform; we see no significant variation in δD_{water} with latitude or with mission, over the 9 year span of these measurements, nor in comparison with previous measurements dating to 1980 [e.g. *Pollock et al.* 1980]. There is no evidence for latitudinally varying injection of stratospheric water or for major temporal or seasonal variations in the mechanism of troposphere-stratosphere exchange. The lack of latitudinal gradient is the expected result if troposphere-stratosphere transport takes place almost exclusively in the tropics; air at higher latitudes will be well-mixed and should show the average stratospheric δD . Fine-scale variability in sources of stratospheric air would then be discernable only in the lower tropical stratosphere. ATMOS data from this region is limited: only four of the ATMOS occultations (28 observations) of this study extend into the lower tropical stratosphere. These data are not sufficient for detection of potential small-amplitude seasonal variation in stratospheric δD_{water} (≈ 40 -50 permil) correlated with seasonal variation in entering water content. They do provide, however, a first approximation of the distribution of δD of entering stratospheric water. Figure 3 shows the distributions of both the lower tropical and total stratospheric δD . Of the limited tropical data, there are no highly depleted points which would suggest injection by gradual ascent. If the tropical data are representative, their consistency suggests that troposphere-stratosphere exchange is dominated by a process with a characteristic isotopic signature similar to the mean stratospheric value.

Conclusions

ATM OS observations of stratospheric deuterated water show that the average water vapor entering the stratosphere is highly depleted of deuterium, with δD_{water} of -680 ± 80 (68% deuterium loss). Model calculations predict, however, that under conditions of thermodynamic equilibrium dehydration to stratospheric mixing ratios should produce depletions of -800-900 (80-90 % deuterium loss). We conclude that water vapor entering the stratosphere has been enriched in deuterium through convective processes. The limited data from the lower tropical stratosphere show little variability from the enriched mean δD_{vapor} , suggesting that contribution by large-scale ascent to total troposphere-stratosphere exchange may be minimal. The enrichment of water vapor ascending to the stratosphere must occur at near-tropopause altitudes; most air entering the stratosphere must have seen convective conditions to at least 14 km. The majority of troposphere-stratosphere exchange must then be associated with tropical deep convection.

Further observations in the lower tropical stratosphere are necessary for determination of whether enrichment occurs above the tropopause, as in penetrative convection models, or just below it. Identification of a seasonal cycle in stratospheric δD_{water} and determination of its amplitude would allow discrimination between two major classes of troposphere-stratosphere transport, and dehydration scenarios: those in which dehydration occurs after enrichment (as in clear-air ascent above clouds, or dehydration by stratospheric wave activity) and those in which condensation occurs before or simultaneously with enrichment (as in evaporation of cumulus-lofted ice particles above the tropopause). We conclude that a high priority should be placed on obtaining tropical measurements of stratospheric H_2O and D_2O , and that further observations should provide substantial additional insight into mechanisms of troposphere-stratosphere transport.

Acknowledgments. We thank Michael Brown for his comments and suggestions on this manuscript, and Nilton Renno for helpful discussions on tropical convection. FJM acknowledges the support of a National Science foundation Graduate Fellowship and a NASA Global Change Graduate Fellowship. This research was supported in part by NASA grant NAGW-413 to the California Institute of Technology.

References

- Abbas, M. M. et al., The hydrogen budget of the stratosphere inferred from ATMOS measurements of H_2O and CH_4 . *Geo. Res. Lett.*, this issue.
- Carli, B. and J. Park, Simultaneous measurement of minor stratospheric constituents with emission far-infrared spectroscopy. *J. Geophys. Res.*, 93, 33851, 1988.
- Danielsen, E. F., A dehydration mechanism for the stratosphere. *Geo. Res. Lett.*, 9, 605, 1982.
- Danielsen, E. F., In situ evidence of rapid, vertical, irreversible transport of lower tropospheric air into the lower tropical stratosphere by convective cloud turrets and by large-scale upwelling in tropical cyclones. *J. Geophys. Res.*, 98, 8665, 1993.
- Dinelli, B. M. et al., Measurement of stratospheric distributions of H_2^{16}O , H_2^{18}O , H_2^{17}O , and H_2^{11}O from fdr-infrared spectra. *J. Geophys. Res.*, 96, 7509, 1991.
- Ehhalt, D. H., Methane in the atmosphere, in *Carbon and the biosphere*, G. M. Woodwell and E. V. Pecan, eds., Atomic Energy Commission, 1973.
- Farmer, C. B., High resolution infrared spectroscopy of the sun and the earth's atmosphere from space. *Mikrochim. Acta*, 119, 189, 1987.
- Gordon, M. R. et al., The Atmospheric Trace Molecular Spectroscopy (ATMOS) experiment deployment on the ATLAS-3 space shuttle mission. *Geo. Res. Lett.*, this issue.
- Holton, J. R., Troposphere-stratosphere exchange. *Reviews of Geophysics*, in press, 1995.
- Hageman, R. et al., Absolute D/H ratio for SMOW. *Tellus*, 22, 712, 1970.
- Irion, F. W. et al., Stratospheric observations of HDO and CH_3D from ATMOS infrared solar spectra. *Geo. Res. Lett.*, this issue.
- Jouzel, J. and L. Merlivat, deuterium and oxygen-18 in precipitation: modeling of the isotopic effects during snow formation. *J. Geophys. Res.*, 89, 11749, 1984.
- Knollenberg, R. G. et al., Measurements of high number densities of ice crystals in the tops of tropical cumulonimbus. *J. Geophys. Res.*, 96, 8639, 1993.
- Knollenberg, R. G. et al., Measurements of the aerosol and ice crystal populations in tropical stratospheric cumulonimbus anvils. *Geo. Res. Lett.*, 9, 613, 1982.
- Majoube, M., Fractionation of oxygen 18 and of deuterium between water and its vapor.

- J. Chem. Phys.*, **68**, 1423, 1971.
- Merlivat, I., and G. Nief, isotopic fractionation of the solid-vapor and liquid-vapor changes of state of water at temperatures below 0°C. *Tellus*, **19**, 122, 1967.
- Newell, R. E. and S. Gould-Stewart, A stratospheric fountain? *J. Atmos. Sci.*, **36**, 2789, 1981.
- Pollock, W. et al., Measurement of stratospheric water vapor by cryogenic collection. *J. Geophys. Res.*, **85**, 5555, 1980.
- Potter, B. E. and J. R. Holton, The role of monsoon convection in dehydration of the lower tropical stratosphere. *J. Atmos. Sci.*, **52**, 1034, 1994.
- Pruppacher, H. R. and J. D. Klett, *Microphysics of clouds and precipitation*, D. Reidel Co., 1980.
- Reid, G. C. and K. S. Gage, On the annual variation in height of the tropical tropopause. *J. Atmos. Sci.*, **38**, 1928, 1981.
- Rinsland, C. F. et al., Stratospheric profiles of heavy water isotopes and CH₃D from analysis of the ATMOS/Sacelab 3 infrared solar spectra. *J. Geophys. Res.*, **96**, 1057, 1991.
- Rinsland, C. F. et al., Simultaneous stratospheric measurements of H₂O, H₂¹⁸O, and CH₄ from balloon-borne and aircraft infrared solar absorption spectra and tunable diode laser laboratory spectra of H₂¹⁸O. *J. Geophys. Res.*, **89**, 7259, 1984.
- Rogers, R. R. and M. K. Yau, *A short course in cloud physics*, Pergamon Press, 1989.
- World Meteorological Organization, *Scientific Assessment of Ozone Depletion*, 1994.

Figure 1. ATMOS measurements of the deuterium content of stratospheric water, given as the fractional change in D/H ratio from standard ocean water, in per mil (O = ocean water; -1000 = complete loss of deuterium). The left panel shows uncorrected observations; the right panel shows the same data with the estimated contribution of 1120 and 1110 from methane oxidation subtracted. The data shown are *approx* 75% of the dataset, filtered at $\text{error}_{\text{H}_2\text{O}} \leq 10\%$, $\text{error}_{\text{CH}_4} \leq 10\%$, and $\text{error}_{\text{HDO}} \leq 30\%$ of the total data points. The solid lines are weighted mean profiles from 15-32 km. $\sigma = 40$ per mil; error with inclusion of systematic errors = 80 per mil.

Figure 2. Model calculations of the isotopic composition of water vapor during ascent to the stratosphere. The upper panel shows the full range of trajectories in conditions of thermodynamic equilibrium, for all possible model parameter values. The solid line represents the case in which all condensate is removed immediately; the dashed line that where all condensate remains with the parcel and cloud glaciation occurs by freezing of droplets at 258-233 K. The lower panel shows the consequences of a fractionation factor modified by supersaturated conditions, for $S = 1, 1.5$, and 2 (right to left). $S=1$ produces cases essentially identical to those above. Solid and dashed lines again represent immediate/delayed removal of condensation, but the glaciation is allowed to proceed by evaporation of droplets and recondensation as ice, producing the strong enhancements seen between 10-12 km: at high S the fractionation for vapor-ice is less than that for vapor-liquid, and deuterium is pumped into the vapor. Complete vapor deposition of ice is not a realistic scenario; the likely real case lies between the extremes presented here.

Figure 3. Histogram of δD values for total stratospheric water (dotted line, representing all points from 15-32 km, and right axis) and for water in the lower tropical stratosphere (solid line, points from 18-27 km at latitudes of ± 25 degrees, left axis). The 28 tropical observations (4 occultations) show a distribution similar to that of the mean stratosphere, with no outlying points that would suggest contributions from different sources of air with differing isotopic compositions. The slight shift of the mean to heavier values in the tropical points may be due to biases in filter 9 H_2O ; see *Abbas et al.* [this issue].





